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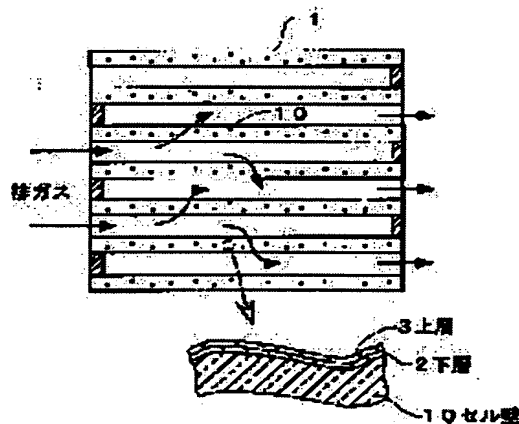
(22)Date of filing : 27.11.2001 (72)Inventor : OGURA YOSHITSUGU

(54) PARTICULATE FILTER

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress the deterioration of combustion performance of a particulate caused by the decrease of a noble metal carrying amount, and also suppress the sulfur poison of an NOX occlusion material.

SOLUTION: A lower layer 2 which is formed by making an oxide carrier carry the NOX occlusion material and noble metal, and an upper layer 3 which is formed by making an oxide having an oxygen storing/discharging capacity carry the noble metal, are formed on a cell wall 10 compartmenting the cells from each other. By separating the upper layer having the function of burning the particulate and the lower layer having the function of controlling NOX emission, the sulfur poison is suppressed, the activity deterioration of noble metal caused by the occlusion material is also suppressed, and the combustion of the particulate is accelerated by including the oxide having the oxygen storing/discharging capacity.



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CLAIMS

[Claim(s)]

[Claim 1] Nothing and these two or more cells are blockaded in the shape of a checker in respect of an end in abbreviation tubed with two or more cells prolonged in parallel mutually. This cell that is not blockaded in respect of the end is the particulate filter which is blockaded in respect of the other end and it comes to blockade in the shape of a checker also in respect of the other end, and to the cell wall which divides these cells. It is NOx to oxide support. Particulate filter characterized by forming the lower layer which comes to support occlusion material and noble metals, the upper layer which comes to support noble metals to the oxide which has oxygen occlusion emission ability, and was formed in this lower layer front face, and the catalyst bed which becomes more.

[Claim 2] the oxide which has said oxygen occlusion emission ability -- CeO₂ and CeO₂-ZrO₂ multiple oxide and CeO₂-ZrO₂-aluminum 2O₃ a multiple oxide -- and -- Particulate filter according to claim 1 which is chosen from Fe 2O₃ and which is a kind at least.

[Claim 3] The amount of support of said noble metals is a particulate filter according to claim 1 with more upper one than a lower layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is arranged on the emission way of a diesel power plant etc., and relates to the particulate filter which has a catalyst function in detail about the particulate filter which carries out uptake of the particulate in exhaust gas.

[0002]

[Description of the Prior Art] In order to carry out uptake of the particulates, such as soot in exhaust gas, the diesel particulate filter (henceforth DPF) is arranged conventionally on the emission way of a diesel power plant. This DPF is formed in a honeycomb configuration from heat-resistant ceramics, such as cordierite, the cel which is not blockaded in respect of the end is blockaded in respect of the other end, and two or more cels (honeycomb path) are blockaded in the shape of a checker also in respect of the other end while being blockaded in the shape of a checker in respect of an end.

[0003] It flows into the outflow side edge side which passes the septum which constitutes a cel from this DPF since that cel is blockaded in respect of the outflow side edge and the exhaust gas which flowed into the inflow side edge side from the cel which carries out opening is difficult to come out from an outflow side edge side as it is, and adjoins out of the cel which is carrying out opening. Therefore, uptake of the particulate in exhaust gas is carried out on a septum or into a septum by the filtration at the time of passing a septum, and the exhaust gas which does not contain a particulate flows out of an outflow side edge side by it.

[0004] By the way, the particulate by which uptake was carried out on a septum or into the septum is deposited gradually, by this, blinding will arise to a septum and ventilation resistance will become large. Then, by heating periodically or passing hot exhaust gas, cleaning which burns the deposited particulate and recovers filtration is performed.

[0005] Then, giving an emission-gas-purification catalyst function to DPF is also performed by it not only burning a particulate, but supporting catalyst metals, such as platinum, to a septum, carrying out oxidative degradation of the hydrocarbon and carbon monoxide in exhaust gas, and understanding some nitrogen oxides a returned part by the catalysis. Thus, since a deposited particulate combustion temperature falls according to DPF which supported the catalyst metal, combustion removal of the particulate can be carried out at exhaust gas temperature, and DPF can be reproduced continuously.

[0006] For example, the continuation playback type DPF which supported alkaline earth metal and a platinum metal to the cell wall of DPF is proposed by JP,7-106290,B. Moreover, in JP,9-094434,A, it is NO_x in the pore of a cell wall. According to [DPF which supported occlusion material is proposed and] this DPF, they are particulate continuation oxidation and NO_x. It is indicated that it can purify.

[0007] However, exhaust gas temperature in the usual transit region from a diesel power plant In order to reproduce continuously 150 to 500 degree C, and the particulate deposited using DPF of the above-mentioned continuation playback type since it was low in exhaust gas, the high oxidation rate was needed in the low exhaust gas temperature field, and the amount of support of noble metals had to be made [many]. Therefore, a price becomes high and DPF of a continuation playback type serves as hindrance of the spread of them.

[0008] Moreover, noble metals and NO_x At the continuation playback type DPF which supported both occlusion material, it is NO_x at the time of use. There is fault that occlusion material moves and

the activity of noble metals falls the front face of noble metals to a wrap sake. Furthermore, it is NO_x. Occlusion material carries out occlusion also of the sulfur oxide in exhaust gas, serves as a sulfate, and is NO_x. There was also a problem that occlusion ability disappeared. This phenomenon is called sulfur poisoning.

[0009]

[Problem(s) to be Solved by the Invention] This invention is NO_x while being made in view of such a situation and controlling the fall of the particulate flammability ability accompanying reduction of the amount of support of noble metals. It aims at controlling sulfur poisoning of occlusion material.

[0010]

[Means for Solving the Problem] The description of the particulate filter of this invention which solves the above-mentioned technical problem Nothing and two or more cels are blockaded in the shape of a checker in respect of an end in abbreviation tubed with two or more cels prolonged in parallel mutually. The cel which is not blockaded in respect of the end is the particulate filter which is blockaded in respect of the other end and it comes to blockade in the shape of a checker also in respect of the other end, and to the cell wall which divides cels It is NO_x to oxide support. It is in the lower layer which comes to support occlusion material and noble metals, the upper layer which came to support noble metals to the oxide which has oxygen occlusion emission ability, and was formed in it on the surface of the lower layer, and the catalyst bed which becomes more being formed.

[0011] the oxide which has oxygen occlusion emission ability -- CeO₂ and CeO₂-ZrO₂ multiple oxide and CeO₂-ZrO₂-aluminum 2O₃ a multiple oxide -- and -- The thing which is chosen from Fe 2O₃ and which is a kind at least is desirable. Moreover, as for the amount of support of noble metals, it is desirable for there to be more upper one than a lower layer.

[0012]

[Embodiment of the Invention] It is NO_x to oxide support in the cell wall which divides cels in the particulate filter of this invention. The lower layer which comes to support occlusion material and noble metals, the upper layer which came to support noble metals to the oxide which has oxygen occlusion emission ability, and was formed in it on the surface of the lower layer, and the catalyst bed which becomes more are formed. Therefore, NO_x Since it is contained only in a lower layer and has not expressed on an emission way, occlusion material is NO_x. The contact probability of occlusion material and a sulfur oxide is reduced, sulfur poisoning can be controlled, and it is NO_x even with after [high] durability. Decontamination capacity is discovered.

[0013] Moreover, since noble metals are supported with the upper layer by the oxide which has oxygen occlusion emission ability, particulate combustion is promoted by the absorption/emission of oxygen. And in the upper layer, it is NO_x. Since occlusion material is not contained, noble metals are NO_x. Fault which is covered by occlusion material and deactivates is prevented, and the activity of noble metals is discovered by max. The amount of support of noble metals can be reduced by this, and suppose that it is cheap. And deposition can be followed, a particulate can be burned and a particulate filter can be reproduced continuously.

[0014] Conventional DPF formed from heat-resistant ingredients, such as cordierite and silicon carbide, can be used for the base of the particulate filter of this invention. What is necessary is just to design the magnitude, the number of cels, porosity, average pore size, etc. according to the purpose.

[0015] The pore of an one to 100 micrometer aperture is formed innumably, and while being able to pass a cell wall from the cel by the side of emission close to the cel by the side of emission appearance, and exhaust gas's being able to circulate and securing permeability because they are open for free passage, it has the structure where a particulate can be filtered at the cell wall which divides two or more cels. And the catalyst bed which becomes a cell wall from a lower layer and the upper layer is formed, and this catalyst bed is formed in the inner circumference front face of the above-mentioned pore, and the inner circumference front face of a cel.

[0016] A lower layer is NO_x supported by oxide support and oxide support. It consists of occlusion material and noble metals. Two or more sorts of multiple oxides chosen from kinds, such as aluminum 2O₃, and TiO₂, ZrO₂, SiO₂, CeO₂, two or more sorts, or these as oxide support can be used. Specific surface area was highly excellent in thermal stability especially. aluminum 2O₃ is desirable. Moreover, if TiO₂ etc. is used, since solid acid nature is strong and contiguity of a sulfur oxide will be controlled, it is NO_x. Sulfur poisoning of occlusion material can be controlled further.

[0017] NO_x supported by the lower layer As occlusion material, it can choose from rare earth metals, such as alkaline earth metal, such as alkali metal, such as K, Na, Li, and Cs, and Ba, calcium, Mg, Sr, and La, Pr, Nd, Sm, and can use. It is NO_x especially. Alkali metal with high occlusion ability is used preferably. Moreover, it is desirable to be able to choose from Pt, Rh, Pd, Ir, Ru, Au, etc., to be able to use as noble metals, and to use Pt with oxidation activity high especially at least.

[0018] As for the lower layer amount of coats, it is desirable to consider as the range per [50-150g] 1l. of filter base objects. It is NO_x if there are few amounts of coats than this range. If occlusion material and the amounts of support of noble metals come to run short and it becomes thicker than this range, the path of the pore which exhaust gas passes will become small, and a pressure loss will increase.

[0019] Moreover, NO_x in a lower layer The amount of support of occlusion material is good to consider as 0.01-0.5 mols per 1l. of filter base objects. NO_x It is NO_x if there are few amounts of support of occlusion material than this. If decontamination capacity runs short and it supports mostly from this, a wrap probability will become high about the noble metals supported by the lower layer, and the activity of noble metals will come to fall.

[0020] And the amount of support of the noble metals in a lower layer has 1 - 3% of the weight of the desirable range to a lower layer. It is NO_x if there are few amounts of support of noble metals than this range. If decontamination capacity runs short and it supports mostly from this, the support consistency within a lower layer is too large, at the time of an elevated temperature, grain growth will come to arise in noble metals, and activity will fall.

[0021] The upper layer consists of an oxide which has oxygen occlusion emission ability, and noble metals supported by this oxide. although this oxide can be used if it has oxygen occlusion emission ability -- CeO₂ and CeO₂-ZrO₂ multiple oxide and CeO₂-ZrO₂-aluminum 2O₃ a multiple oxide -- and -- Especially the thing that is chosen from Fe 2O₃ and that is a kind at least is desirable. It is because especially these oxides are excellent in oxygen occlusion emission ability and it excels also in endurance.

[0022] It is desirable to be able to choose from Pt, Rh, Pd, Ir, Ru, Au, etc., to be able to use as noble metals supported by the upper layer, and to use Pt with oxidation activity high especially at least.

[0023] As for the upper amount of coats, it is desirable to consider as the range of per [10-50g] 1l. of filter base objects. If there are few amounts of coats than this range, the amounts of support of noble metals come to run short, if it becomes thicker than this range, the path of the pore which exhaust gas passes will become small, and a pressure loss will increase. Moreover, since exhaust gas stops being able to reach a lower layer easily, it is NO_x. Decontamination capacity will also fall.

[0024] In order to raise particulate oxidation activity, as for the amount of support of the noble metals in the upper layer, it is desirable to make [many] it, 1 - 10% of the weight of its range is desirable to the upper layer, and especially its 5 % of the weight or more is more desirable than a lower layer. If there are few amounts of support of noble metals than this range, particulate oxidation ability runs short of, if it supports mostly from this, the support consistency within the upper layer will be too large, and activity will fall with the grain growth at the time of an elevated temperature. The same noble metals as a lower layer may be supported, and different noble metals can also be supported.

[0025] After slushing the slurry of the above-mentioned oxide powder in a cel from an end side, making it adhere to a cell wall by drawing in from an other end side and calcinating it in order to form a lower layer or the upper layer for example, it is the noble metals or NO_x of the specified quantity. What is necessary is just to support occlusion material. Moreover, it can also be made to adhere to a cell wall similarly using the slurry formed from the oxide powder which supported noble metals beforehand.

[0026]

[Example] Hereafter, an example and the example of a comparison explain this invention concretely.

[0027] (Example 1) The outline configuration of the particulate filter of this example is shown in drawing 1 . This particulate filter consists of a base 1 which consists of cordierite, a lower layer 2 formed in the cell wall 10 of a base 1, and the upper layer 3 formed in the front face of a lower layer 2. The base 1 is making the honeycomb configuration in which the cel with which opening was

carried out to the inflow side edge side, and the outflow side edge side was taken up in checkers, and the cel which an inflow side edge side is taken up in checkers, and carries out opening in respect of an outflow side edge were formed by turns. In addition, the important section enlarged drawing of the cell wall 10 in drawing 1 R> 1 shows the interior of the pore which can pass exhaust gas. Hereafter, the manufacture approach of this particulate filter is explained and it replaces with detailed explanation of a configuration.

[0028] As a base 1, it is a diameter. 100mm, die length 150mm DPF made from cordierite was prepared. The average pore size of this DPF is 30 micrometers, and porosity is 60%.

[0029] To a degree 2Oaluminum₃ powder The 100 weight sections and TiO₂ powder After mixing the 100 weight sections, the ZrO₂ powder 20 weight section, the alumina sol 3 weight section as a binder, and the ion-exchange-water 40 weight section, preparing a slurry and being filled up in a cel from the emission close side edge side of DPF, it drew in from the emission appearance side edge side, and was made to adhere to a cell wall. After that It dries at 120 degrees C for 2 hours. It calcinated at 500 degrees C for 2 hours, and the bottom coat layer was formed. A bottom coat layer is per [of DPF] l. It is 120g.

[0030] Then, the nitric-acid solution of the dinitrodiammine platinum of predetermined concentration is prepared, after DPF with a bottom coat layer is immersed, it pulls up, and an excessive drop is dried at blowing off and 120 degree C for 2 hours. It calcinated at 500 degrees C for 1 hour, and Pt was supported in the bottom coat layer. To a bottom coat layer, the amount of support of Pt is 1 % of the weight, and is per [of DPF] l. It is 1.2g.

[0031] it is made to sink into DPF which furthermore has the bottom coat layer which supported Pt for the potassium acetate of predetermined concentration, and the specified quantity of the mixed water solution of an acetic-acid lithium -- 120 degree C -- after 2-hour desiccation It calcinated at 500 degrees C for 1 hour, and K and Li were supported. This formed the lower layer 2. DPF is K per l. 0.2 mols and Li 0.1 mols were supported.

[0032] On the other hand, after a mean diameter prepares CeO₂ powder which is about 1 micrometer and sinks in the specified quantity of the nitric-acid solution of the dinitrodiammine platinum of predetermined concentration, evaporation to dryness is carried out. Pt/CeO₂ powder which calcinated at 500 degrees C for 1 hour, and supported Pt was prepared. The amount of support of Pt is 5 % of the weight.

[0033] The ceria sol and ion exchange water as this Pt/CeO₂ powder and a binder are mixed, and a slurry is prepared, and after being filled up in a cel from the inflow side edge side of DPF in which the lower layer 2 was formed, it drew in from the outflow side edge side, and was made to adhere to the front face of a lower layer 2. After that It dries at 120 degrees C for 2 hours. It calcinated at 500 degrees C for 2 hours, and the upper layer 3 was formed. About 30g per l. of DPF is formed, and, for Pt, DPF is [the upper layer 3] abbreviation per l. 1.5g is supported. That is, the amount of support of Pt per l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 2.7g.

[0034] (Example 2) A lower layer 2 and the upper layer 3 were formed like the example 1 except having made the amount of support of Pt of a lower layer 2 into 2 % of the weight to the lower layer 2. The amount of support of Pt per 1l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 3.9g.

[0035] (Example 3) A lower layer 2 is received in the amount of support of Pt of a lower layer 2. A lower layer 2 and the upper layer 3 were formed like the example 1 except having considered as 2.9 % of the weight. The amount of support of Pt per 1l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 5.0g.

[0036] (Example 4) It is abbreviation to the upper layer 3 about having made the amount of support of Pt of a lower layer 2 into 2 % of the weight to the lower layer 2, and the amount of support of Pt of the upper layer 3. A lower layer 2 and the upper layer 3 were formed like the example 1 except having considered as 8.7 % of the weight. The amount of support of Pt per 1l. of DPF is abbreviation by the sum total of a lower layer and the upper layer. It is 5.0g.

[0037] (Example 5) A lower layer 2 is received in the amount of support of Pt of a lower layer 2. A lower layer 2 and the upper layer 3 were formed like the example 1 except having considered as 3.9 % of the weight, and having made the amount of support of Pt of the upper layer 3 into about 1 % of the weight to the upper layer 3. The amount of support of Pt per 1l. of DPF is abbreviation by the

sum total of a lower layer and the upper layer. It is 5.0g.

[0038] (Example 1 of a comparison) A lower layer 1 is formed like an example 1, and it replaces with CeO₂ powder. The upper layer 2 was formed like the example 1 except having used 2Oaluminum₃ powder. The amount of support of Pt per 1l. of DPF is the same abbreviation as an example 1 by the sum total of a lower layer and the upper layer. It is 2.7g.

[0039] (Example 2 of a comparison) It is the amount of formation of a bottom coat layer per 1l. of DPF. Having been referred to as 150g, and the amount of support of Pt in a bottom coat layer Except having considered as 3.3 % of the weight, the lower layer 2 was formed like the example 1, and this was made into the particulate filter of the example 2 of a comparison. The amount of support of Pt per 1l. of DPF It is 5.0g.

[0040] <A trial and evaluation> It is displacement about each above-mentioned filter. It attaches in the exhaust air system of the diesel power plant of 4.2L, respectively, and is entering gas temperature. The durability test of 50 hours was performed at 650 degrees C. Next, each filter after a durability test is attached in the exhaust air system of the diesel power plant of displacement 2L, respectively, and it is entering gas temperature. It operated at 350 degrees C for 3 hours. They are a discharge per unit time amount of a diesel particulate at this time (W0), and 2.9 g/an hour.

[0041] Each filter after the above-mentioned trial It dried at 120 degrees C for 4 hours, and the weight (W1) was measured, respectively. In subsequently, the inside of an electric furnace The diesel particulate which heated for 2 hours and has been deposited at 500 degrees C was burned, and subsequent weight (W2) was measured, respectively. From these values, by the degree type, the combustion rate of a diesel particulate is computed, respectively and a result is shown in Table 1.

[0042]

each filter after measuring combustion rate (%) = (W1-W2) / (3xW0)) x 100, next a combustion rate is again attached in the exhaust air system of the diesel power plant of displacement 2L, respectively -- the exhaust gas burned on condition that [rich] A/F=12 -- entering -- gas temperature 600 degrees C -- for 15 minutes -- passing -- NO_x NO_x by which occlusion was carried out to occlusion material Reduction desorption was carried out. After that It changes to Lean operation of A/F=35 and is entering gas temperature. NO_x in 300 degrees C The amount of occlusion was measured. A result is shown in Table 1.

[0043]

[Table 1]

| | 下 層 | | | | 上 層 | | | 全体の Pt担持量 (g/L) | 燃焼率 (%) | NO _x 吸蔵量 (mg/L) |
|-------|--------------------------------|---------------|------------------------|----------------|--------------------------------|---------------|----------------|-----------------------|------------|-------------------------------|
| | 酸化物 | コート量 (g/L) | NO _x 吸蔵材 | Pt担持量 (重量%) | 酸化物 | コート量 (g/L) | Pt担持量 (重量%) | | | |
| 実施例 1 | | | | 1.0 | CeO ₂ | | 5.0 | 2.7 | 72 | 290 |
| 実施例 2 | Al ₂ O ₃ | 120 | K:0.2 mg/L | 2.0 | CeO ₂ | 30 | 5.0 | 3.9 | 81 | 320 |
| 実施例 3 | + | | | 2.9 | CeO ₂ | | 5.0 | 5.0 | 86 | 390 |
| 実施例 4 | TiO ₂ | | | 2.0 | CeO ₂ | | 8.7 | 5.0 | 93 | 340 |
| 実施例 5 | + | | | 3.9 | CeO ₂ | | 1.0 | 5.0 | 60 | 310 |
| 比較例 1 | ZrO ₂ | 150 | mg/L | 1.0 | Al ₂ O ₃ | | 5.0 | 2.7 | 66 | 180 |
| 比較例 2 | | | | 3.3 | — | — | — | 5.0 | 58 | 260 |

[0044] compared with the example 3 of a comparison which is the conventional configuration, the inflammable ability of a diesel particulate is boiling the filter of examples 1-4 markedly, and is improving. This is considered that it has contributed greatly that the active spot of Pt in the upper layer 3 exists mostly also in after elevated-temperature durability and that the oxygen from CeO₂ was supplied with the filter of each example. The effectiveness of CeO₂ is clear also from the result of an example 1 and the example 1 of a comparison.

[0045] NO_x It is NO_x after durability, so that there are many amounts of support of lower layer Pt fundamentally, since occlusion reduction is performed in a lower layer. The amount of occlusion increases. However, it compares with the example 2 of a comparison, and the filter of examples 1-5 is NO_x after durability. There are many amounts of occlusion and the correlation with the amount of support of Pt is not seen here. That is, for the filter of an example, the amount of support of Pt is

NOx at least than the example 2 of a comparison. There are many amounts of occlusion and CeO₂ of the upper layer 3 is NOx. Having controlled sulfur poisoning of occlusion material is guessed..

[0046] If the amount of support of Pt of the upper layer 3 is made fewer than a lower layer 2 still like an example 5, it is also distinct that the inflammable ability of a diesel particulate is falling.

[0047]

[Effect of the Invention] That is, it is NOx while the fall of the inflammable ability of a diesel particulate accompanying reduction of the amount of support of noble metals is controlled according to the particulate filter of this invention. Sulfur poisoning of occlusion material is also controlled.

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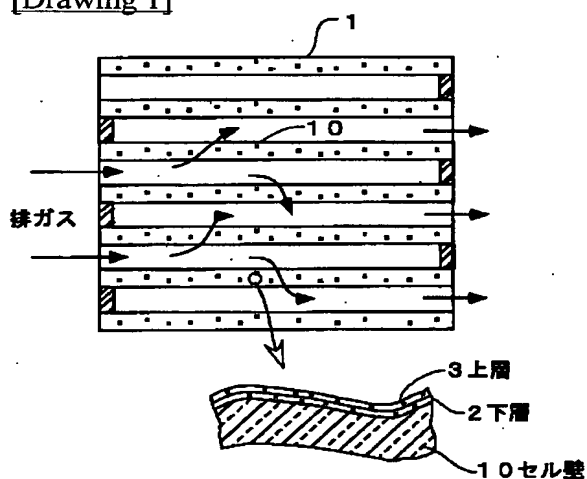
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DRAWINGS

[Drawing 1]



[Translation done.]

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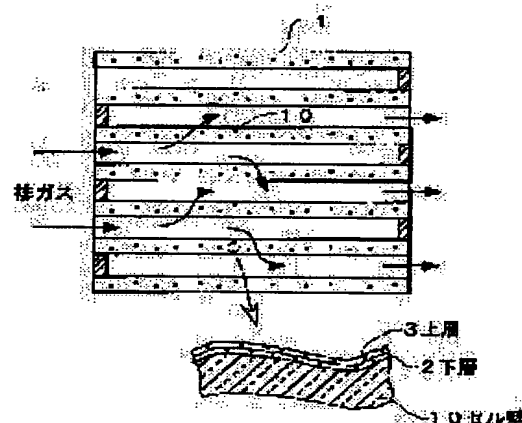
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(54) PARTICULATE FILTER

(57)Abstract

PROBLEM TO BE SOLVED: To suppress the deterioration of combustion performance of a particulate caused by the decrease of a noble metal carrying amount, and also suppress the sulfur poison of an NOX occlusion material.

SOLUTION: A lower layer 2 which is formed by making an oxide carrier carry the NOX occlusion material and noble metal, and an upper layer 3 which is formed by making an oxide having an oxygen storing/discharging capacity carry the noble metal, are formed on a cell wall 10 comparting the cells from each other. By separating the upper layer having the function of burning the particulate and the lower layer having the function of controlling NOX emission, the sulfur poison is suppressed, the activity deterioration of noble metal caused by the occlusion material is also suppressed, and the combustion of the particulate is accelerated by including the oxide having the oxygen storing/discharging capacity.



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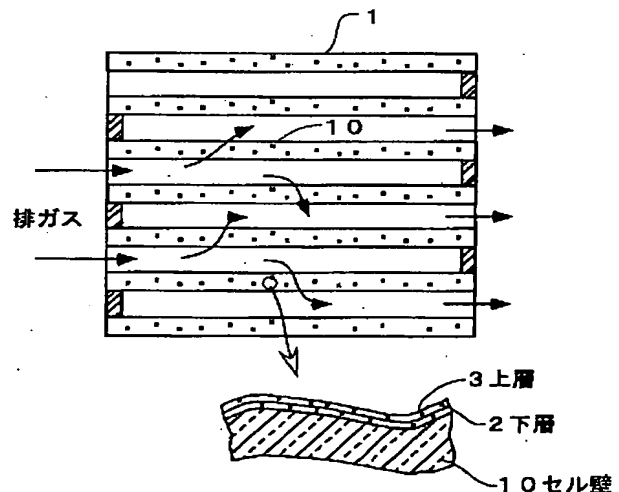
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(54) 【発明の名称】 パティキュレートフィルタ

(57) 【要約】

【課題】 貴金属の担持量の低減に伴うパティキュレートの燃焼性能の低下を抑制するとともに、NO_x吸蔵材の硫黄被毒も抑制する。

【解決手段】 セルどうしを区画するセル壁10に、酸化物担体にNO_x吸蔵材と貴金属とを担持してなる下層2と、酸素吸蔵放出能を有する酸化物に貴金属を担持してなる上層3を形成した。パティキュレートを燃焼させる機能をもつ上層と、NO_x浄化能をもつ下層とに分離することで硫黄被毒を抑制できるとともにNO_x吸蔵材による貴金属の活性低下が抑制され、上層に酸素吸蔵放出能を有する酸化物を有することでパティキュレートの燃焼が促進される。



【特許請求の範囲】

【請求項 1】 互いに平行に延びる複数のセルをもつ略筒状をなし、複数の該セルは一端面で市松模様状に閉塞され、一端面で閉塞されていない該セルが他端面で閉塞されて他端面でも市松模様状に閉塞されてなるパティキュレートフィルタであって、

該セルどうしを区画するセル壁には、酸化物担体にNO_x吸蔵材と貴金属とを担持してなる下層と、酸素吸蔵放出能を有する酸化物に貴金属を担持してなり該下層の表面に形成された上層と、よりなる触媒層が形成されていることを特徴とするパティキュレートフィルタ。

【請求項 2】 前記酸素吸蔵放出能を有する酸化物は、CeO₂、CeO₂-ZrO₂複合酸化物、CeO₂-ZrO₂-Al₂O₃ 複合酸化物、及び Fe₂O₃から選ばれる少なくとも一種である請求項 1 に記載のパティキュレートフィルタ。

【請求項 3】 前記貴金属の担持量は上層の方が下層より多い請求項 1 に記載のパティキュレートフィルタ。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、ディーゼルエンジンの排ガス流路などに配置され、排ガス中のパティキュレートを捕集するパティキュレートフィルタに関し、詳しくは触媒機能を有するパティキュレートフィルタに関する。

【0002】

【従来の技術】 ディーゼルエンジンの排ガス流路には、排ガス中の煤などのパティキュレートを捕集するために、従来よりディーゼルパティキュレートフィルタ

(以下、DPFという) が配置されている。このDPFは、コーゼライトなどの耐熱性セラミックスからハニカム形状に形成され、複数のセル(ハニカム通路)は一端面で市松模様状に閉塞されるとともに、一端面で閉塞されていないセルが他端面で閉塞されて他端面でも市松模様状に閉塞されている。

【0003】 このDPFでは、流入側端面に開口するセルから流入した排ガスは、そのセルは流出側端面で閉塞されているためそのまま流出側端面から出ることは困難であるので、セルを構成する隔壁を通過して隣接する流出側端面に開口しているセルから流出する。したがって隔壁を通過する際の濾過作用により、排ガス中のパティキュレートは隔壁上あるいは隔壁中に捕集され、流出側端面からはパティキュレートを含まない排ガスが流出する。

【0004】 ところで隔壁上あるいは隔壁中に捕集されたパティキュレートは次第に堆積し、これによって隔壁に目詰まりが生じて通気抵抗が大きくなってしまう。そこで定期的に加熱したり高温の排ガスを通過させることによって、堆積したパティキュレートを燃焼させ濾過作用を回復させるクリーニングが行われている。

【0005】 そこで隔壁に白金などの触媒金属を担持

し、その触媒作用によってパティキュレートを燃焼するばかりでなく、排ガス中の炭化水素や一酸化炭素を酸化分解し、窒素酸化物の一部を還元分解することによって、DPFに排ガス浄化触媒機能をもたせることも行われている。このように触媒金属を担持したDPFによれば、堆積したパティキュレートの燃焼温度が低下するので、排ガス温度でパティキュレートを燃焼除去することができ、DPFを連続的に再生することができる。

【0006】 例えば特公平7-106290号公報には、DPFのセル壁にアルカリ土類金属と白金族金属とを担持した連続再生式DPFが提案されている。また特開平9-094434号公報には、セル壁の細孔内にNO_x吸蔵材を担持したDPFが提案され、このDPFによればパティキュレートの連続酸化とNO_xの浄化とを行うことができると記載されている。

【0007】 ところがディーゼルエンジンからの通常走行域での排ガス温度は 150～500℃と低いために、上記した連続再生式のDPFを用いて堆積したパティキュレートを排ガス中で連続的に再生するためには、低排ガス温度領域で高い酸化速度が必要となり、貴金属の担持量を多くせざるを得なかった。そのため連続再生式のDPFは価格が高くなり、それが普及の妨げとなっている。

【0008】 また貴金属とNO_x吸蔵材の両方を担持した連続再生式DPFでは、使用時にNO_x吸蔵材が移動して貴金属の表面を覆うために、貴金属の活性が低下するという不具合がある。さらにNO_x吸蔵材は排ガス中の硫黄酸化物をも吸蔵し、硫酸塩となってNO_x吸蔵能が消失するという問題もあった。この現象は硫黄被毒と称されている。

【0009】

【発明が解決しようとする課題】 本発明はこのような事情に鑑みてなされたものであり、貴金属の担持量の低減に伴うパティキュレート燃焼性能の低下を抑制するとともに、NO_x吸蔵材の硫黄被毒も抑制することを目的とする。

【0010】

【課題を解決するための手段】 上記課題を解決する本発明のパティキュレートフィルタの特徴は、互いに平行に延びる複数のセルをもつ略筒状をなし、複数のセルは一端面で市松模様状に閉塞され、一端面で閉塞されていないセルが他端面で閉塞されて他端面でも市松模様状に閉塞されてなるパティキュレートフィルタであって、セルどうしを区画するセル壁には、酸化物担体にNO_x吸蔵材と貴金属とを担持してなる下層と、酸素吸蔵放出能を有する酸化物に貴金属を担持してなり下層の表面に形成された上層と、よりなる触媒層が形成されていることにある。

【0011】 酸素吸蔵放出能を有する酸化物は、CeO₂、CeO₂-ZrO₂複合酸化物、CeO₂-ZrO₂-Al₂O₃ 複合酸化物、及び Fe₂O₃から選ばれる少なくとも一種であること

が望ましい。また貴金属の担持量は、上層の方が下層より多いことが望ましい。

【0012】

【発明の実施の形態】本発明のバティキュレートフィルタでは、セルどうしを区画するセル壁に、酸化物担体に NO_x 吸蔵材と貴金属とを担持してなる下層と、酸素吸蔵放出能を有する酸化物に貴金属を担持してなり下層の表面に形成された上層と、よりなる触媒層が形成されている。したがって NO_x 吸蔵材は下層のみに含まれ排ガス流路に表出していないので、 NO_x 吸蔵材と硫黄酸化物との接触確率が低減され、硫黄被毒を抑制することができ耐久後も高い NO_x 浄化能が発現される。

【0013】また上層では、酸素吸蔵放出能を有する酸化物に貴金属が担持されているため、酸素の吸放出によってバティキュレートの燃焼が促進される。そして上層には NO_x 吸蔵材が含まれていないので、貴金属が NO_x 吸蔵材で覆われて失活するような不具合が防止され、貴金属の活性が最大に発現される。これにより貴金属の担持量を低減することができ、安価とすることができる。そしてバティキュレートを堆積に連続して燃焼することができ、バティキュレートフィルタを連続的に再生することができる。

【0014】本発明のバティキュレートフィルタの基体には、コーゼライト、炭化ケイ素などの耐熱性材料から形成された従来のDPFを用いることができる。その大きさ、セル数、気孔率、平均細孔径などは目的に応じて設計すればよい。

【0015】複数のセルを区画するセル壁には、孔径 $1 \sim 100 \mu\text{m}$ の細孔が無数に形成され、それらが連通することで、排ガス流入側のセルから排ガス流出側のセルへセル壁を通過して排ガスが流通可能であり、通気性を確保するとともにバティキュレートを濾過できる構造となっている。そしてセル壁には下層と上層とからなる触媒層が形成され、この触媒層は上記細孔の内周表面とセルの内周表面に形成されている。

【0016】下層は、酸化物担体と、酸化物担体に担持された NO_x 吸蔵材及び貴金属とから構成されている。酸化物担体としては、 Al_2O_3 、 TiO_2 、 ZrO_2 、 SiO_2 、 CeO_2 、などの一種又は複数種、あるいはこれらから選ばれる複数種の複合酸化物などを用いることができる。中でも比表面積が高く熱安定性に優れた Al_2O_3 が好ましい。また TiO_2 などを用いれば、固体酸性が強いことから硫黄酸化物の近接が抑制されるため、 NO_x 吸蔵材の硫黄被毒をさらに抑制することができる。

【0017】下層に担持される NO_x 吸蔵材としては、K、Na、Li、Csなどのアルカリ金属、Ba、Ca、Mg、Srなどのアルカリ土類金属、La、Pr、Nd、Smなどの希土類金属の中から選択して用いることができる。中でも NO_x 吸蔵能が高いアルカリ金属が好ましく用いられる。また貴金属としては、Pt、Rh、Pd、Ir、Ru、Auなどから選択し

て用いることができ、中でも酸化活性が高いPtを少なくとも用いることが好ましい。

【0018】下層のコート量は、フィルタ基体1リットルあたり $50 \sim 150 \text{ g}$ の範囲とすることが好ましい。コート量がこの範囲より少ないと NO_x 吸蔵材及び貴金属の担持量が不足するようになり、この範囲より厚くなると排ガスが通過する細孔の径が小さくなって圧損が増大する。

【0019】また下層における NO_x 吸蔵材の担持量は、フィルタ基体1リットルあたり $0.01 \sim 0.5 \text{ mol}$ とするのがよい。 NO_x 吸蔵材の担持量がこれより少ないと NO_x 浄化能が不足し、これより多く担持すると、下層に担持された貴金属を覆う確率が高くなり貴金属の活性が低下するようになる。

【0020】そして下層における貴金属の担持量は、下層に対して $1 \sim 3 \text{ 重量\%}$ の範囲が好ましい。貴金属の担持量がこの範囲より少ないと NO_x 浄化能が不足し、これより多く担持すると、下層内での担持密度が大き過ぎて高温時に貴金属に粒成長が生じるようになり活性が低下する。

【0021】上層は、酸素吸蔵放出能を有する酸化物と、この酸化物に担持された貴金属とから構成される。この酸化物は酸素吸蔵放出能を有すれば用い得るが、 CeO_2 、 $\text{CeO}_2\text{-ZrO}_2$ 複合酸化物、 $\text{CeO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3$ 複合酸化物、及び Fe_2O_3 から選ばれる少なくとも一種であることが特に好ましい。これらの酸化物は酸素吸蔵放出能に特に優れ、かつ耐久性にも優れているからである。

【0022】上層に担持される貴金属としては、Pt、Rh、Pd、Ir、Ru、Auなどから選択して用いることができ、中でも酸化活性が高いPtを少なくとも用いることが好ましい。

【0023】上層のコート量は、フィルタ基体1リットルあたり $10 \sim 50 \text{ g}$ の範囲とすることが好ましい。コート量がこの範囲より少ないと貴金属の担持量が不足するようになり、この範囲より厚くなると排ガスが通過する細孔の径が小さくなって圧損が増大する。また排ガスが下層に到達しにくくなるため NO_x 浄化能も低下してしまう。

【0024】上層における貴金属の担持量は、バティキュレートの酸化活性を高めるために下層より多くすることが好ましく、上層に対して $1 \sim 10 \text{ 重量\%}$ の範囲が好ましく、 5 重量\% 以上が特に好ましい。貴金属の担持量がこの範囲より少ないとバティキュレートの酸化能に不足し、これより多く担持すると上層内での担持密度が大き過ぎて高温時の粒成長によって活性が低下する。下層と同一の貴金属を担持してもよいし、異なる貴金属を担持することもできる。

【0025】下層又は上層を形成するには、例えば上記酸化物粉末のスラリーを一端面からセル内に流し込み、他端面から吸引することでセル壁に付着させ、それを焼

成した後に所定量の貴金属あるいは NO_x 吸蔵材を担持すればよい。また、予め貴金属を担持した酸化粉末から形成されたスラリーを用いて同様にセル壁に付着させることもできる。

【0026】

【実施例】以下、実施例及び比較例により本発明を具体的に説明する。

【0027】（実施例1）図1に本実施例のパティキュレートフィルタの概略構成を示す。このパティキュレートフィルタは、コーゼライトよりなる基体1と、基体1のセル壁10に形成された下層2と、下層2の表面に形成された上層3とから構成されている。基体1は流入側端面に開口し流出側端面が市松状に塞がれたセルと、流入側端面が市松状に塞がれ流出側端面で開口するセルとが交互に形成されたハニカム形状をなしている。なお図1におけるセル壁10の要部拡大図は、排ガスが通過可能な細孔の内部を示している。以下、このパティキュレートフィルタの製造方法を説明し、構成の詳細な説明に代える。

【0028】基体1として、直径100mm、長さ150mmのコーゼライト製のDPFを用意した。このDPFの平均細孔径は $30\mu\text{m}$ であり、気孔率は60%である。

【0029】次に Al_2O_3 粉末100重量部と、 TiO_2 粉末100重量部と、 ZrO_2 粉末20重量部と、バインダとしてのアルミナゾル3重量部及びイオン交換水40重量部を混合してスラリーを調製し、DPFの排ガス流入側端面からセル内に充填した後に排ガス流出側端面から吸引してセル壁に付着させた。その後120℃で2時間乾燥し500℃で2時間焼成して下コート層を形成した。下コート層はDPFの1リットルあたり120gである。

【0030】続いて所定濃度のジニトロジアンミン白金の硝酸溶液を用意し、下コート層をもつDPFを浸漬した後引き上げて余分な液滴を吹き払い、120℃で2時間乾燥し500℃で1時間焼成して、下コート層にPtを担持した。Ptの担持量は、下コート層に対して1重量%であり、DPFの1リットルあたり1.2gである。

【0031】さらに所定濃度の酢酸カリウムと酢酸リチウムの混合水溶液の所定量を、Ptを担持した下コート層をもつDPFに含浸させ、120℃で2時間乾燥後500℃で1時間焼成してKとLiを担持した。これにより下層2を形成した。DPFの1リットルあたりKは0.2モル、Liは0.1モル担持された。

【0032】一方、平均粒径が約 $1\mu\text{m}$ の CeO_2 粉末を用意し、所定濃度のジニトロジアンミン白金の硝酸溶液の所定量を含浸した後、蒸発乾固し500℃で1時間焼成してPtを担持したPt/ CeO_2 粉末を調製した。Ptの担持量は5重量%である。

【0033】このPt/ CeO_2 粉末とバインダとしてのセリアゾル及びイオン交換水を混合してスラリーを調製し、下層2が形成されたDPFの流入側端面からセル内に充

填した後に流出側端面から吸引して下層2の表面に付着させた。その後120℃で2時間乾燥し500℃で2時間焼成して上層3を形成した。上層3はDPFの1リットルあたり約30g形成され、PtはDPFの1リットルあたり約1.5g担持されている。すなわちDPFの1リットルあたりのPtの担持量は、下層及び上層の合計で約2.7gである。

【0034】（実施例2）下層2のPtの担持量を下層2に対して2重量%としたこと以外は実施例1と同様にし、下層2と上層3を形成した。DPF1リットルあたりのPtの担持量は、下層及び上層の合計で約3.9gである。

【0035】（実施例3）下層2のPtの担持量を下層2に対して2.9重量%としたこと以外は実施例1と同様にし、下層2と上層3を形成した。DPF1リットルあたりのPtの担持量は、下層及び上層の合計で約5.0gである。

【0036】（実施例4）下層2のPtの担持量を下層2に対して2重量%としたこと、上層3のPtの担持量を上層3に対して約8.7重量%としたこと以外は実施例1と同様にし、下層2と上層3を形成した。DPF1リットルあたりのPtの担持量は、下層及び上層の合計で約5.0gである。

【0037】（実施例5）下層2のPtの担持量を下層2に対して3.9重量%としたこと、上層3のPtの担持量を上層3に対して約1重量%としたこと以外は実施例1と同様にし、下層2と上層3を形成した。DPF1リットルあたりのPtの担持量は、下層及び上層の合計で約5.0gである。

【0038】（比較例1）実施例1と同様にし下層1を形成し、 CeO_2 粉末に代えて Al_2O_3 粉末を用いたこと以外は実施例1と同様にし上層2を形成した。DPF1リットルあたりのPtの担持量は、下層及び上層の合計で実施例1と同様の約2.7gである。

【0039】（比較例2）下コート層の形成量をDPF1リットルあたり150gとしたこと、及び下コート層中のPtの担持量を3.3重量%としたこと以外は実施例1と同様にし下層2を形成し、これを比較例2のパティキュレートフィルタとした。DPF1リットルあたりのPtの担持量は5.0gである。

【0040】＜試験・評価＞上記した各フィルタを排気量4.2Lのディーゼルエンジンの排気系にそれぞれ取付け、入りガス温度650℃で50時間の耐久試験を行った。次に耐久試験後の各フィルタを排気量2Lのディーゼルエンジンの排気系にそれぞれ取付け、入りガス温度350℃で3時間運転した。この時のディーゼルパティキュレートの単位時間あたりの排出量(W_0)は、2.9g/時間である。

【0041】上記試験後の各フィルタを120℃で4時間乾燥し、その重量(W_1)をそれぞれ測定した。次いで電

気炉中にて 500℃で 2 時間加熱して堆積しているディーゼルパティキュレートに燃焼し、その後の重量 (W_2) をそれぞれ測定した。これらの値から、次式によってディーゼルパティキュレートの燃焼率をそれぞれ算出し、結果を表 1 に示す。

【0042】

$$\text{燃焼率 (\%)} = ((W_1 - W_2) / (3 \times W_0)) \times 100$$

次に、燃焼率を測定後の各フィルタを再び排気量 2 L の*

* ディーゼルエンジンの排気系にそれぞれ取付け、A/F=12 のリッチ条件で燃焼させた排ガスを入りガス温度 600℃で 15 分間流して、NO_x 吸蔵材に吸蔵された NO_x を還元脱離させた。その後 A/F=35 のリーン運転に切り替え、入りガス温度 300℃における NO_x 吸蔵量を測定した。結果を表 1 に示す。

【0043】

【表 1】

| | 下 層 | | | | 上 層 | | | 全体の Pt 担持量 (g/L) | 燃焼率 (%) | NO _x 吸蔵量 (ng/L) |
|-------|--------------------------------|---------------|---------------------------------|-----------------|--------------------------------|---------------|-----------------|------------------------|------------|-------------------------------|
| | 酸化物 | コート量 (g/L) | NO _x 吸蔵材 | Pt 担持量 (重量%) | 酸化物 | コート量 (g/L) | Pt 担持量 (重量%) | | | |
| 実施例 1 | | 120 | K:0.2 mg/L Li:0.1 mg/L | 1.0 | CeO ₂ | 30 | 5.0 | 2.7 | 72 | 290 |
| 実施例 2 | Al ₂ O ₃ | | | 2.0 | CeO ₂ | | 5.0 | 3.9 | 81 | 320 |
| 実施例 3 | + | | | 2.9 | CeO ₂ | | 5.0 | 5.0 | 86 | 390 |
| 実施例 4 | TiO ₂ | | | 2.0 | CeO ₂ | | 8.7 | 5.0 | 93 | 340 |
| 実施例 5 | + | | | 3.9 | CeO ₂ | | 1.0 | 5.0 | 60 | 310 |
| 比較例 1 | ZrO ₂ | 150 | | 1.0 | Al ₂ O ₃ | — | 5.0 | 2.7 | 66 | 180 |
| 比較例 2 | | | | 3.3 | — | | — | 5.0 | 58 | 260 |

【0044】実施例 1～4 のフィルタは、従来の構成である比較例 3 に比べてディーゼルパティキュレートの燃焼性能が格段に向上している。これは、各実施例のフィルタでは高温耐久後においても上層 3 における Pt の活性点が多く存在していること、及び CeO₂ からの酸素が供給されたことが大きく寄与していると考えられる。CeO₂ の効果は、実施例 1 と比較例 1 の結果からも明らかである。

【0045】NO_x の吸蔵還元は下層で行われるので、基本的には下層の Pt の担持量が多いほど耐久後の NO_x 吸蔵量が多くなる。しかし実施例 1～5 のフィルタは比較例 2 に比べて耐久後の NO_x 吸蔵量が多く、ここには Pt の担持量との相関関係は見られない。つまり実施例のフィルタは Pt の担持量が比較例 2 より少なくても NO_x 吸蔵量が多く、上層 3 の CeO₂ が NO_x 吸蔵材の硫黄被毒を抑制して ※

※ いることが推察される。

【0046】さらに実施例 5 のように上層 3 の Pt の担持量を下層 2 よりも少なくすると、ディーゼルパティキュレートの燃焼性能が低下していることも明らかである。

【0047】

【発明の効果】すなわち本発明のパティキュレートフィルタによれば、貴金属の担持量の低減に伴うディーゼルパティキュレートの燃焼性能の低下が抑制されるとともに、NO_x 吸蔵材の硫黄被毒も抑制される。

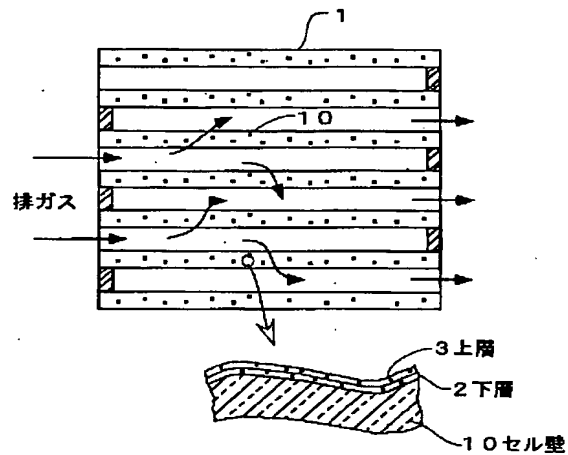
【図面の簡単な説明】

【図 1】本発明の一実施例のパティキュレートフィルタの概略構成を示す説明図である。

【符号の説明】

1 : 基体 2 : 下層 3 : 上層 1
0 : セル壁

【図1】



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